215° (214–216°).[18] A mixture melting point with an authentic sample of the hydrochloric acid salt of benzylphenylamine, m.p. 214.5–216°, melted at 213–215°.

Reaction of N-Nitrosodibenzylamine with Lithium in Liquid Ammonia.—To a stirred solution of 1.54 g. (0.22 g. atom) of lithium dissolved in 250 ml. of liquid ammonia was added dropwise a solution of 10.0 g. (0.044 mole) of N-nitrosodibenzylamine in 125 ml. of dry ether and 25 ml. of dry dioxane. External cooling was removed and after 10 minutes color change from blue to white then from orange to bright red was observed. The red reaction was stirred for 1.5 hours and then hydrolyzed with 50 ml. of ethanol followed by 50 ml. of water. The reaction mixture was poured into 500 ml. of water, extracted with ether and the extracts dried over magnesium sulfate. Removal of solvent yielded 5.0 g. of residue.

At this point, in another experiment, 6% of tribenzylhydrazine, m.p. 82.5–84° (m.p. 86°)[8] was isolated by crystallization from the residue. A picrate salt was prepared in ether, m.p. 138–140.5 (m.p. 140–141°).[8]

The mixture was extracted with dry Skellysolve B several times and the extracts chromatographed through neutral alumina (Woelm, activity one). A Skellysolve B-insoluble material was recrystallized from ethanol, 0.50 g., m.p. 205–207°. This solid contains nitrogen and an infrared spectrum exhibited a strong absorption at 6.08 μ, probably C=N.[19] The solid reacts slowly with a methanolic hydrochloric acid solution of 2,4-dinitrophenylhydrazine to give

(18) W. S. Emerson and P. M. Walters, This Journal, 60, 2023 (1938); K. Brand, Ber., 42, 3460 (1909).

(19) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 226.

an orange derivative, m.p. 118–121°. The solid was not further characterized.

The first 25-ml. fraction obtained from the column, using dry Skellysolve B as eluent, yielded 0.32 g. (4%) of bibenzyl, m.p. 50–51.5°; a mixture melting point with authentic bibenzyl melted at 50–52°. The next three fractions yielded 1.75 g. (37.5%) of benzylamine, whose picrate salt prepared in ether, melted at 197–200° (195–199°).[20] A mixture melting point with the picrate salt of authentic benzylamine melted at 197.5–200°. A yellow band was removed from the column, using dry methanol as eluent, yielding 1.3 g. (15%) of dibenzylamine, whose picrate salt prepared in ether melted at 139–141°. A mixture melting point with the picrate salt of authentic dibenzylamine prepared in ether melted at 138.5–140°.

The picrate salt of authentic dibenzylamine was prepared by adding excess saturated picric acid in ether to an ether solution of the amine. Three separate preparations of this salt using various samples of dibenzylamine all yielded a yellow solid, m.p. 140°. The previously reported[8] picrate of dibenzylamine could not be duplicated. An analytical sample was prepared by recrystallization from ethanol to yield yellow needles, m.p. 140–141° (93–94°).[8]

Anal.[21] Calcd. for $C_{20}H_{18}N_4O_7$: C, 56.34; H, 4.25; N, 13.14. Found: C, 56.48; H, 4.61; N, 13.19.

(20) G. Jerusalem, J. Chem. Soc., 95, 1283 (1909).

(21) Analyses by Schwarzkopf Laboratories, New York, N. Y.

BROOKLYN 1, N. Y.

Pyrolysis of Pyruvic Acid Hydrazones[1]

BY J. H. BOYER AND L. R. MORGAN, JR.

Thermal decarboxylation of pyruvic acid hydrazones (I) through zwitterions provides a basis for understanding the formation of both acetaldehyde and, in some cases, biacetyl derivatives. When the hydrazone terminal nitrogen is weakly basic, zwitterions of type III predominate and decarboxylation leads to the formation of corresponding acetaldehyde and biacetyl hydrazones. The formation of the phenylhydrazone (X) of α-acetylquinoline upon decarboxylation of pyruvic acid phenylhydrazone (Ib) in quinoline establishes the presence of an intermediate (VIb) capable of reacting with cationoid reagents. For those hydrazones in which terminal nitrogen is more strongly basic, it is proposed that decarboxylation proceeds through β,γ-azobetaines (IV) with the formation of acetaldehyde but not of biacetyl hydrazones. With the respective loss of ammonia and aniline, the bis-hydrazone at 170° and the bis-phenylhydrazone of biacetyl at 300° undergo ring-closure condensation into 4,5-dimethyltriazole and 2-phenyl-4,5-dimethyltriazole. The latter also is obtained from the monophenylhydrazone monoxime of biacetyl at 200°. At 160° a mixture of α- and β-acetaldehyde phenylhydrazones is transformed quantitatively into the β-modification (lower melting).

A bis-phenylhydrazone (VIII) of biacetyl was reported in 1888[2] as a product from thermal decarboxylation of pyruvic acid phenylhydrazone (Ib). The present work, undertaken to explain its formation, developed into an investigation on the thermal decarboxylation of five pyruvic acid hydrazones. Other products from Ib included carbon dioxide, ammonia and the phenylhydrazones Vb of acetaldehyde.[2] These have now also been obtained by carrying out the decarboxylation in inert solvents. From pyruvic acid dinitrophenylhydrazone (Ic) the best yield (60%) of biacetyl, isolated as its bis-dinitrophenylhydrazone, and the lowest yield of acetaldehyde, isolated as its dinitrophenylhydrazone, have been obtained. In contrast only the corresponding acetaldehyde derivatives are ob-

(1) Partial support of this work under a National Institutes of Health Grant No. CY-2895-CY is gratefully acknowledged.

(2) E. Fischer and F. Jourdan, Ber., 16, 2241 (1883); F. R. Japp and F. Klingemann, Ann., 247, 222 (1888); J. Chem. Soc., 53, 519 (1888).

tained from pyruvic acid hydrazone (Ia), α-methyl-α-phenylhydrazone (Id) and diphenylhydrazone (Ie).
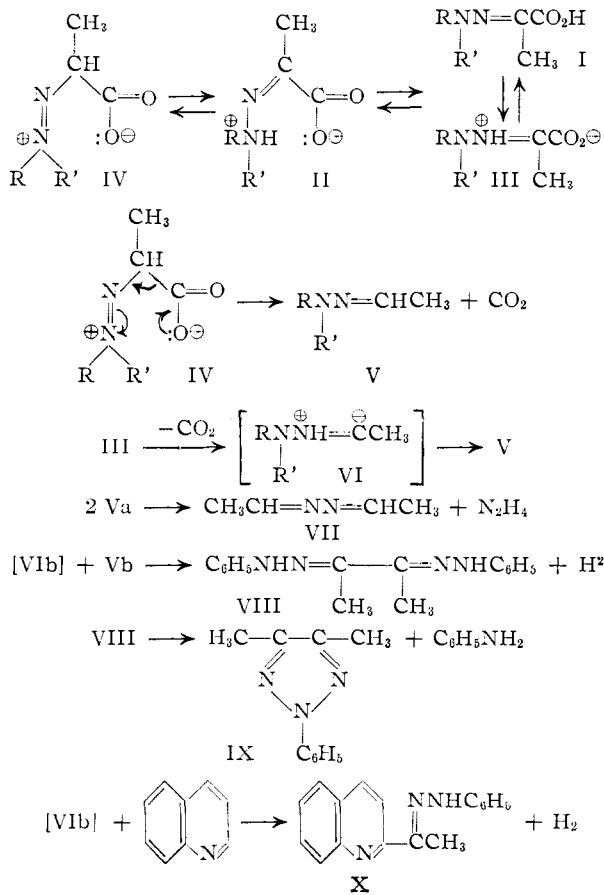
Interpretation of the data has been based upon an ionic process for thermal decarboxylation of carboxylic acids as an established rule and the prediction that decarboxylation of a zwitterion will require less activation energy than of a corresponding acid anion.[3] The ratio (II/III) of the two zwitterionic forms for pyruvic acid hydrazones is dependent upon relative basicities of the hydrazone nitrogen atoms. For those hydrazones with weakly basic terminal nitrogen, zwitterions III may predominate in decarboxylation. It is predicted that hydrazones I with no demonstrable basicity at terminal nitrogen will decarboxylate exclusively through zwitterions of type III. For those hydrazones in which the terminal nitrogen is appreciably basic an additional equilibrium with an

(3) R. D. Brown, Quart. Revs., 5, 131 (1951).

azobetaine (IV) is available. This shift to β,γ-unsaturation is probably thermodynamically favorable insofar as the quaternary sp^3 nitrogen (II) becomes planar (sp^2) in IV and in certain examples resonance interaction with an attached aromatic ring helps to counterbalance destabilization through loss of conjugation with the carboxyl group.[4]

$$CH_3-CH-N\diagdown C=O \;/\; \oplus N :O^\ominus \quad (IV)$$

$$CH_3-C-N\diagdown C=O \;/\; RNH :O^\ominus \quad (II)$$

$$RNN=CCO_2H \;/\; R'\; CH_3 \quad (I)$$

$$RNNH=CCO_2^\ominus \;/\; R'\; CH_3 \quad (III)$$

$$CH_3-CH-N\diagdown C=O \;/\; \oplus N :O^\ominus \quad (IV) \longrightarrow RNN=CHCH_3 + CO_2 \quad (V)$$

$$III \xrightarrow{-CO_2} \left[RNNH=CCH_3 \;/\; R'\; (VI) \right] \longrightarrow V$$

$$2\ Va \longrightarrow CH_3CH=NN=CHCH_3 + N_2H_4 \quad (VII)$$

$$[VIb] + Vb \longrightarrow C_6H_5NHN=C-C=NNHC_6H_5 \;/\; CH_3\; CH_3 + H_2 \quad (VIII)$$

$$VIII \longrightarrow H_3C-C-C-CH_3 + C_6H_5NH_2 \quad (IX,\ C_6H_5)$$

$$[VIb] + \text{(naphthyl)} \longrightarrow \text{(naphthyl)} \begin{array}{c} NNHC_6H_5 \\ CCH_3 \end{array} + H_2 \quad (X)$$

a, R = R' = H; b, R = H, R' = C₆H₅; c, R = H, R' = 2,4(NO₂)₂C₆H₃; d, R = CH₃, R' = C₆H₅; e, R = R' = C₆H₅

The role of β,γ-olefinic and azomethine unsaturation in decarboxylation has been amply described. Thermal decarboxylation of α,β-unsaturated acids through the thermodynamically less stable β,γ-isomers,[5] decarboxylation of α-pyridylacetic acids[6,7] and heavy metal cation catalyzed decarboxylation of Schiff bases derived from pyridoxal and α-

amino acids[8] have been understood to proceed through cyclic intermediates in which at least three pairs of electrons shifted. Decarboxylation of azoisobutyric acid (β,γ-azo unsaturation) followed by hydrolysis affords α-hydrazinoisobutyric acid and acetone.[9] This decarboxylation can also be understood to proceed through a cyclic intermediate.

$$KO_2CC(CH_3)_2N=NC(CH_3)_2CO_2K \xrightarrow{H_3O^\oplus} $$

$$HO_2CC(CH_3)_2N \diagdown \begin{array}{c} CH_3\ CH_3 \\ C \\ C=O \end{array} \xrightarrow{-CO_2}$$

$$HO_2CC(CH_3)_2NN=C(CH_3)_2 \xrightarrow{H_3O^\oplus} HO_2CC(CH_3)_2NHNH_2 + (CH_3)_2CO$$

Thermal decarboxylation of pyruvic acid hydrazone (Ia, d) in which terminal nitrogen is electron rich[10] presumably occurs predominantly through the corresponding azobetaines IVa,d. In contrast with Id an unusually high temperature (300°) is required for thermal decarboxylation of Ia and has been attributed in part to destabilization of IVa through loss of conjugation. Both the unknown hydrazone (Va) of acetaldehyde and the unknown azine of pyruvic acid are possible intermediates in the formation of acetaldehyde azine VII. From the failure to detect the azine of pyruvic acid in experiments which allowed incomplete thermal decarboxylation of Ia and the failure to prepare it by

(8) D. E. Metzler, M. Ikawa and E. E. Snell, THIS JOURNAL, 76, 648 (1954).

(9) J. Thiele and K. Heuser, Ann., 290, 37 (1896). These authors also found that hydrazoisobutyric acid required heating above 200° for decomposition. The important product of this pyrolysis was later identified as 2,2,5,5-tetramethylpiperazinedione-3,6 by S. Gabriel, Ber., 44, 59 (footnote 3) (1911). The reaction may now be explained

$$HO_2CC(CH_3)_2N \diagdown \begin{array}{c} CH_3\ CH_3 \\ C \\ NH\; C=O \end{array} \xrightarrow{-CO_2} \begin{array}{c} (CH_3)_2C=NH \\ + \\ HO_2CC(CH_3)_2NH_2 \end{array}$$

$$2\ HO_2CC(CH_3)_2NH_2 \xrightarrow{-2\ H_2O} (H_3C)_2C \diagdown \begin{array}{c} H \\ N \\ C=O \\ C(CH_3)_2 \\ N \\ H \end{array}$$

$$(CH_3)_2C=NH \xrightarrow{H_2O} (CH_3)_2C=O + NH_3$$

The earlier workers observed the formation of ammonia, carbon dioxide and an "inflammable gas" which we may now suspect was acetone.

(10) The more basic terminal nitrogen in N,N-dimethylhydrazones (P. A. S. Smith and E. E. Most, Jr., J. Org. Chem., 22, 358 (1957)) and benzaldehyde hydrazone (J. Thiele, Ann., 376, 239 (1910)) is exclusively methylated. H. F. Harnsberger, E. L. Cochran and H. H. Szmant, THIS JOURNAL, 77, 5048 (1955), measured the basicities of hydrazones of aryl ketones using trichloroacetic acid in anhydrous methanol. The results were interpreted in terms of a transition state, $R_2CN=NH_2...H...O_2CCCl_3$, which required terminal nitrogen to be more basic.
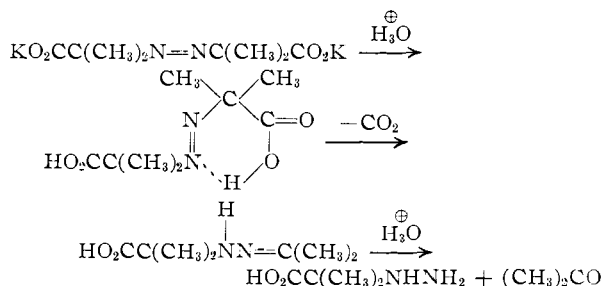
(4) To what extent an equilibrium exists between azo derivatives and hydrazones has not been clearly established. In many cases, acid catalysis has brought about isomerization of azo derivatives into hydrazones. That the reverse process may also occur in at least trace amounts was demonstrated in the confirmed formation of phenylazomethane from phenylhydrazine and formaldehyde (E. C. C. Baly and W. B. Tuck, J. Chem. Soc., 89, 986 (1906); H. Stobbe and R. Nowak, Ber., 47, 578 (1914)). On the basis of ultraviolet light absorption Baly and Tuck claimed that phenylhydrazones of acetaldehyde, propionaldehyde, acetone, diethyl ketone and acetophenone upon exposure to light changed into azo isomers.

(5) R. T. Arnold, O. C. Elmer and R. M. Dodson, THIS JOURNAL, 72, 4359 (1950); R. T. Arnold and M. J. Danzig, ibid., 79, 892 (1957).

(6) W. von E. Doering and V. F. Pasternak, ibid., 72, 143 (1950).

(7) K. Auwers and A. Boennecke, Ann., 378, 254 (1910), reported the following surprisingly stable acids with α,β- and or β,γ-azomethine unsaturation: C₆H₅CON(C₆H₅)N=C(CH₃)CH₂CO₂H, m.p. 203°, no decomposition, and C₆H₅CON(C₆H₅)N=C(CO₂H)C(CH₃)=N-NHC₆H₅, m.p. 110–111°, no decomposition.
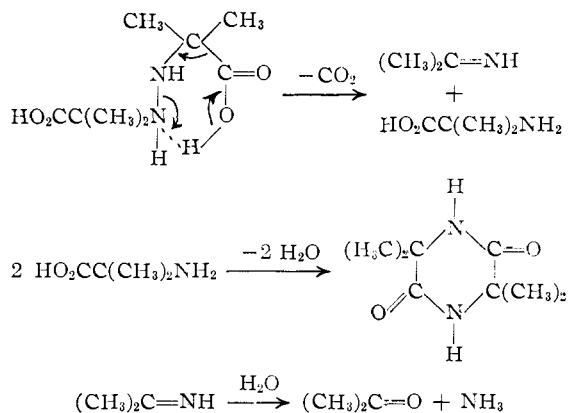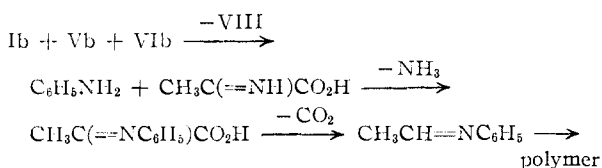
heating an excess of pyruvic acid with hydrazine, we have concluded that Va was more probable. It is well known that attempts to prepare this hydrazone from acetaldehyde and hydrazine have led instead to azine formation.

By analogy with decarboxylation of picolinic and quinaldic acids,[3] intermediates capable of reacting with cationoid reagents are to be expected from decarboxylation through III. Support for the assumption that formation of a bis-phenyl-hydrazone of biacetyl (VIII) results from nucleophilic attack of VIb upon Vb (intermediate and product from decarboxylation of zwitterion IIIb) has been found in the formation of the phenylhydrazone X of α-acetylquinoline when the decarboxylation of Ib was carried out in quinoline. In this case the phenylhydrazones Vb but not VIII were also formed. It was reported that benzaldehyde phenylhydrazone was obtained upon pyrolysis of phenylglyoxylic acid phenylhydrazone.[11] Insofar as benzil derivatives, ammonia, aniline and benzonitrile were not reported, the intermediate zwitterion, $C_6H_5N^{\oplus}H{=}NCH(C_6H_5)CO_2^{\ominus}$ (type IV), played the predominant role in decarboxylation. It is surprising that pyruvic acid diphenylhydrazone (Ie) does not afford biacetyl bis-diphenyl-hydrazone upon decarboxylation. An explanation for its apparently exclusive decarboxylation through IVe lies in the increased stabilization of the azobetaine IVe through conjugation with two attached phenyl groups.

Formation of ammonia upon decarboxylation of Ib but not Ia, d, e presumably depends upon hydrogenolysis of Ib at the nitrogen to nitrogen bond as the formation of VIII and hydrogen occurs.[12] It is assumed that aniline and the imine of pyruvic acid, the expected hydrogenolysis products, in a subsequent condensation afforded ammonia and pyruvic acid anil and decarboxylation of the latter gave acetaldehyde anil which polymerized. This explanation requires a limiting yield of one-third mole each for VIII and ammonia per mole of Ib. The isolation of ammonia in 37.5% and VIII in 39% of this amount has provided an indication that decarboxylation through IIIb occurs at a minimum of 13%. The absence of both ammonia and 2,4-dinitroaniline upon decarboxylation of Ic is attributed to preferential reduction of nitro groups.

$$Ib + Vb + VIb \xrightarrow{-VIII}$$

$$C_6H_5NH_2 + CH_3C({=}NH)CO_2H \xrightarrow{-NH_3}$$

$$CH_3C({=}NC_6H_5)CO_2H \xrightarrow{-CO_2} CH_3CH{=}NC_6H_5 \longrightarrow$$
$$polymer$$

Formation of pyridylcarbinols upon pyrolysis of picolinic acid in aromatic aldehydes[3] suggested an investigation of the pyrolysis of pyruvic acid phenylhydrazone in benzaldehyde. Decarboxylation occurs at 160–170°, but the phenylhydrazone of phenylacetylcarbinol is not found. Carbonyl ex-

change brings about the formation of the phenylhydrazone of benzaldehyde.

Both α- and β-modifications of the phenylhydrazone Vb of acetaldehyde were isolated using chromatographic separation on alumina. In accordance with a quantitative transformation of a prepared mixture of α- and β-forms at 160° for six hours into the β-isomer, the yield of the α-, or higher melting, isomer upon pyrolysis of Ib decreased as the reaction time was prolonged.[13,14]

Apparently the bis-hydrazone of biacetyl undergoes polymerization[15] to a certain extent upon being heated. A competing reaction affords 4,5-dimethyl-1,2,3-triazole and ammonia. In similar ring-closure condensations, pyrolysis of either a bis-phenylhydrazone VIII or a monophenylhydrazone monoxime of biacetyl produces 2-phenyl-4,5-dimethyl-1,2,3-triazole (IX) together with aniline or water, respectively. Accordingly, prolonged heating of pyruvic acid phenylhydrazone allowed biacetyl phenylhydrazone to be detected as the corresponding triazole and aniline.

Experimental

Pyrolysis of Pyruvic Acid Hydrazones.—In a flask, equipped with condenser and gas trap, 35.1 g. (0.197 mole) of the phenylhydrazone, m.p. 188–192° dec.,[2] was heated at 155° until gas evolution was completed (about 2.5 hours). Carbon dioxide, 6.50 g. (74.5%), was isolated as calcium carbonate (14.7 g.); and ammonia (0.49 g.), collected in ether saturated with hydrogen chloride, as ammonium chloride (1.53 g.), m.p. 330–331° (sublimation), which was titrated against standard sodium hydroxide. A deep amber oil, 18.3 g., and a yellow solid, 6.97 g., remained. Upon distillation, the oil separated into a light yellow unidentified liquid (probably acetaldehyde anil), 1.2 g., b.p. 100–105° (40 mm.), which rapidly turned dark and polymerized: a yellow solid, 3.3 g., b.p. 130–139° (40 mm.); a deep yellow solid, 6.6 g., b.p. 150–160° (40 mm.); and a deep orange solid residue, 6.5 g. The distilled solids were eluted from an alumina column using a mixture of 90% chloroform and 10% benzene and then recrystallized from ethanol. The lower-boiling solid separated as yellow needles, 1.1 g. (4%), m.p. and mixture m.p. with β-phenylhydrazone of acetaldehyde 55.5–56°.[13] The higher-boiling solid separated from ethanol as yellow needle clusters, 4.2 g. (16%), m.p. and mixture m.p. with α-phenylhydrazone of acetaldehyde 97–98°.[13,16] The bis-phenylhydrazone of biacetyl, 6.7 g. (25%), was obtained as an amorphous yellow powder upon reprecipitating from benzene the combined solid residues from the reaction mixture and the distillation. Both the m.p. and the mixture m.p. was 247–248°.[3]

Pyrolysis of 5 to 90% solutions of pyruvic acid phenylhydrazine in tetralin, decalin or o-dichlorobenzene at 155–160° for 2.5 hours occurred with the same products and yields described above for dry pyrolysis. An increase in the yield of β-phenylhydrazone of acetaldehyde was observed by allowing longer reaction time at 160°. This was in agreement with the quantitative transformation of a mixture, m.p. 72.5–74°, of α- and β-phenylhydrazones of acetalde-

(11) A. Elbers, *Ann.*, **227**, 340 (1885).

(12) The ease of hydrogenolysis of the nitrogen–nitrogen bond in hydrazines and hydrazones has been demonstrated by the use of Raney nickel in the absence of added hydrogen (R. L. Hinman, *J. Org. Chem.*, **22**, 148 (1957)). See also R. Ciusa, *Gazz. chim. ital.*, **51**, II, 49 (1921).

(13) G. Lockemann and O. Liesche, *Ann.*, **342**, 28 (1905), reported the acid-catalyzed transformation from α- to β-form and the base-catalyzed transformation from β- to α-form.

(14) It has been claimed[2] that the bis-phenylhydrazone of biacetyl was formed in small amounts upon heating acetaldehyde phenylhydrazone at 180–190°. Our attempts to repeat this work were unsuccessful.

(15) Biacetyl and hydrazine at room temperature gave a polymeric azine (B. G. Zimmermann and H. L. Lochte, THIS JOURNAL, **58**, 948 (1936)).

(16) E. G. Laws and N. V. Sidgwick, *J. Chem. Soc.*, **99**, 2087 (1911), reported α-modification, b.p. 236–237° (20 mm.) and the β-modification, b.p. 133–136° (20 mm.). The conclusion that the two forms differ widely in volatility (T. W. J. Taylor and W. Baker, Sidgwick's "Organic Chemistry of Nitrogen," Oxford University Press, London, 1937 (corrected 1945), p. 397) is in error.

TABLE I

PYROLYSIS OF PYRUVIC ACID HYDRAZONES

Hydra-zone	M.p., °C.	Pyrolysis temp., °C.	Time, hr.	CO_2, % yield	Acetaldehyde derivative, (% yield)	M.p., °C.	Biacetyl derivative, (% yield)	M.p., °C.
Ia	112[a]	315	3	78.5	VII (48)	B. 86–87[b]	(0)	.....
Ib	188–192 d.	155	2.5	74.5	Vb (20)	α, 97–98	VIII (25)	247–248
						β, 55.5–56		
Ic	213[c] d.	210	3	78	Vc (30)	168.5[c,d]	DNP (60)	309[c,d]
Id	80[e]	170	2.5	86	Vd (41)[f]	B. 136–137[g]	(0)	.....
Ie	145[h]	170	2.5	89	Ve (62)	60–61[i]	(0)	.....

[a] Th. Curtius and H. Long, *J. prakt. Chem.*, [2] **44**, 555 (1891), reported 115–117°.   [b] B.p. (1 atm.); Th. Curtius and E. Zinkeisen, *ibid.*, [2] **58**, 325 (1898), reported 95–96°; A. Kurrmann, *Compt. rend.*, **217**, 148 (1943), reported b.p. 86–87°, $n^{26.5}$D 1.4485. A refractive index n^{25}D 1.4364 was observed here. This azine prepared from acetaldehyde and hydrazine boiled at 86–87°, n^{21}D 1.4360.   [c] C. F. H. Allen, THIS JOURNAL, **52**, 2955 (1930).   [d] Acetaldehyde DNP and biacetyl DNP in equimolar amounts form a eutectic, m.p. 112–114°, which may be separated upon elution from alumina with a mixture of benzene (1 part) and chloroform (1 part).   [e] E. Fischer and F. Jourdan, *Ber.*, **16**, 2241 (1883).   [f] n^{26}D 1.4120.   [g] B.p. (25 mm.); H. R. Stevens and F. W. Ward, *J. Chem. Soc.*, **125**, 1328 (1924).   [h] W. v. Miller and J. Plöchl, *Ber.*, **25**, 2063 (1892).   [i] E. Fischer and O. Hess, *ibid.*, **17**, 567 (1884).

hyde (from acetaldehyde and phenylhydrazine) at 150–165° for six hours into the β-isomer, m.p. 57°.

In another run, carried out over a period of 8 hours at 155–160°, the amber oil was directly separated using an alumina column. Eluting with a mixture of 10% benzene and 90% chloroform allowed the separation of 3.2 g. (12%) of α-acetaldehyde phenylhydrazone, m.p. 98°, and 2.1 g. (8%) of β-acetaldehyde phenylhydrazone, m.p. 56°. The remaining material upon removal from the column was stripped of solvent and steam distilled. From the benzene extract of the distillate, 2.52 g. (this requires a minimum yield of 29% for the bis-phenylhydrazone of biacetyl) of aniline, b.p. 183–186°, hydrochloride, m.p. 196–197°, was isolated by distillation. From the residue 2.61 g. of 2-phenyl-4,5-dimethyltriazole, b.p. 254.5–257°,[17] m.p. and mixture m.p. 34–35°,[17] was isolated by distillation.

The other hydrazones were pyrolyzed in a similar manner. Results are found in Table I. In all cases, solid products were identified using mixture melting point determinations.

Upon heating 6.42 g. (0.036 mole) of pyruvic acid phenylhydrazone in 45 ml. (0.44 mole) of freshly distilled benzaldehyde for three hours at 155–170°, ammonia and carbon dioxide in trace amounts were evolved. After removal of excess benzaldehyde, the residue recrystallized from ethanol as yellow needles, 2.1 g. (29.7%), of **benzaldehyde phenylhydrazone**, m.p. and mixture m.p. 157–158°. Under similar conditions the phenylhydrazone of benzophenone was quantitatively recovered and benzaldehyde was quantitatively recovered from a benzaldehyde solution of acetaldehyde phenylhydrazone at 160–170° for three hours. In the latter experiment acetaldehyde phenylhydrazone decomposed and/or polymerized into unidentified material.

(17) H. v. Pechmann, *Ber.*, **21**, 2751 (1888).

In an excess of quinoline pyrolysis of pyruvic acid phenylhydrazone afforded 2 to 5% yields of the phenylhydrazone of α-acetylquinoline, m.p. and mixed m.p. 152–156°.[18] Both α- (m.p. 97–98°) and β- (m.p. 55.5–56°) isomers of acetaldehyde phenylhydrazone were isolated in small amounts.

4,5-Dimethyltriazole.—Upon heating 6.5 g. (0.057 mole) of a bis-hydrazone of biacetyl, m.p. 157°,[19] at 170° for 2.5 hours, ammonia, 0.92 g. (70%), was evolved and collected in ethereal hydrogen chloride as ammonium chloride, sublimation at 330–331°, 2.81 g. A red yellow oil, 1.8 g., reprecipitated from benzene as a deep yellow solid with no melting point but gradual decomposition from 100 to 300°.[15] A light yellow solid, 2.16 g. (25%) upon recrystallization from absolute ethanol, was identified as 3,4-dimethyltriazole trihydrate, m.p. 97.5–98°.[20]

2-Phenyl-4,5-dimethyltriazole (IX) was prepared in a similar manner from 6.0 g. (0.023 mole) of a bis-phenylhydrazone of biacetyl, m.p. 309°, at 300° for 2.5 hours. Aniline, 2.0 g., was quantitatively obtained as its hydrochloride, 2.7 g., m.p. 196–197°, and the product recrystallized from benzene as a yellow amorphous powder, 2.0 g. (51%). It was identical with 2-phenyl-4,5-dimethyltriazole, m.p. and mixed m.p. 34–35°, obtained from the monoxime monophenylhydrazone of biacetyl, m.p. 158°,[17] at 200° for 2 hours.

NEW ORLEANS 18, LA.

(18) An authentic sample was prepared according to H. Meyer, *ibid.*, **46**, 2931 (1913).

(19) Th. Curtius and K. Thun, *J. prakt. Chem.*, [2] **44**, 174 (1891).

(20) H. v. Pechmann and W. Bauer, *Ber.*, **42**, 659 (1909).